

KINETICS OF THE GAS PHASE PYROLYSIS OF CHLORINE PENTAFLUORIDE¹

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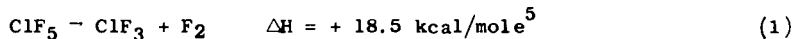
The kinetics of the photochemical formation of chlorine pentafluoride from ClF_3 and F_2 has been studied recently by Krieger, Gatti, and Schumacker.² We report herein the results of our investigation of the gas phase thermal decomposition of ClF_5 .

EXPERIMENTAL

The electrically-heated stirred flow reactor (91-ml, monel) employed is described elsewhere.^{3,4} Chlorine pentafluoride vapor of 98 weight percent purity (containing about 1.3% HF and 0.7% ClF_3) was passed through the reactor at an initial partial pressure of 32 mm in a mixture with helium. The total pressure was 1 atm. The reactor was equipped with a by-pass to allow measurement of the ClF_5 concentration in the entering gas stream.

The gases leaving the reactor (or the by-pass) were passed through a 10-cm nickel infrared cell with AgCl windows. The ClF_5 concentration was followed by measuring the absorbance at 12.5 microns. The flow rates were measured with a soap bubble flow meter connected to the exit stream. The measured flow rates and reactor volume were corrected to reactor temperature. No correction was made for the partial dissolution of reactants and products in the soap solution or for the presence of water vapor.

Infrared analysis of the exit gas showed ClF_3 and ClF_5 as the major absorbers, with ClF present in trace quantities. Fluorine does not absorb in this range (2-15 microns). These results indicate that the stoichiometry is mainly:



RESULTS

The results obtained for the thermal decomposition of ClF_5 over the temperature range 252-307° are presented in Table 1. For a stirred flow reactor, the rate constants for a simple order, single-reactant reaction are given by the equation:

$$k_n = (P^0 - P) / (P^n \tau) \quad (2)$$

where P^0 and P are the partial pressures, respectively, of reactant entering and

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1. This work was supported by the United States Air Force under Contract No. AFO4(611)-10544.
 2. R. L. Krieger, R. Gatti, and H. J. Schumacker, *Z. Phys. Chem.*, **51**, 240 (1966).
 3. J. M. Sullivan and T. J. Houser, *Chem. Ind. (London)*, 1057 (1965).
 4. J. M. Sullivan and A. E. Axworthy, *J. Phys. Chem.*, **70**, 3366 (1966).
 5. JANAF Thermochemical Tables, Quarterly Supplement No. 7.

leaving the reactor, τ , is the average residence time in the reactor, and n is the order of the reaction.⁴ It can be shown from eq 2 that for a first-order reaction, a plot of $\alpha/(1-\alpha)$ vs τ , where α is the fraction reacted, should be linear with a slope equal to the rate constant. Figure 1 shows that the decomposition of ClF_5 follows first-order kinetics up to 80% reaction at 293°. The data in Figure 1 were obtained at temperatures of 291.5-294.0°, and corrected to 293.0° using an activation energy of 41 kcal/mole. The rate constant, k_1 , from each experiment is listed in Table 1. The best first-order rate constant, k_1^A , at each temperature, obtained from a plot of the type shown in Figure 1, is given in the last column of Table 1 and plotted in the Arrhenius form in Figure 2. A least squares fit of the data to the Arrhenius expression yields the line shown in Figure 2 which represents the rate expression:

$$k_1 = 10^{14.61} \exp(-41,330/RT) \text{ sec}^{-1} \quad (3)$$

The uncertainty in activation energy is about 2 kcal/mole.

The mixing requirements for a stirred flow reactor do not allow a convenient procedure for varying widely the surface-to-volume ratio, but the high values of the activation energy and preexponential factor suggest that the reaction is homogeneous in nature. Also, it was found that the rates were unchanged after the reactor, containing products of reaction, had been allowed to sit at 280° for 1 month.

DISCUSSION

Three possible mechanisms may be written which are compatible with the observed rate expression, i.e., first order in ClF_5 with no apparent inhibition as the products accumulate:

A) Unimolecular Elimination of F_2



B) Non Chain Radical Mechanism



C) Long Chain Radical Mechanism



The long chain mechanism (C) may be questioned on the basis of the observed rate parameters A and E. Mechanism (C) requires that

$$A = \left(\frac{A_5 A_6 A_7}{A_8} \right)^{\frac{1}{2}} \quad \text{and} \quad E = \frac{1}{2} (E_5 + E_6 + E_7 - E_8)$$

The A factors for the individual steps can be estimated from the generalizations proposed by Benson and Demore⁶. Thus,

$$\left(\frac{A_5 A_6 A_7}{A_8}\right)^{\frac{1}{2}} \sim \left(\frac{10^{14} 10^{14} 10^{10}}{10^{10}}\right)^{\frac{1}{2}} \sim 10^{14}. \text{ This value is in good agreement with the}$$

observed value of $10^{14.6}$. $E_5 + E_7$ are assumed equal to $\Delta H^\circ + E_{-7}$, where ΔH° is the heat of reaction for $\text{ClF}_5 \rightarrow \text{ClF}_3 + 2\text{F}$ ($\Delta H^\circ = 57 \text{ KCal/mole}$)⁴ and E_{-7} is the activation energy for the reverse of reaction (7). Semenov's approximation⁷ gives $E_{-7} = 2.5 \text{ KCal/mole}$ and $E_6 = 11.0 \text{ KCal/mole}$. The radical-radical

reactions (-5) and (8) are assumed to have zero activation energies. Therefore $E = \frac{1}{2}(57.0 + 2.5 + 11.0) \sim 35 \text{ KCal/mole}$. This value is somewhat lower than the observed value of 40.3 KCal/mole and suggests that the long chain mechanism (C) probably is not important in the decomposition of ClF_5 .

Unfortunately the data do not allow a choice to be made between the molecular elimination mechanism (A) and the non chain mechanism (B). Thermochemical data⁵

$$\text{give } K_{eq} = 10^{-8.85} \frac{18.5}{10^9} \text{ for the reverse of reaction (4). Therefore,}$$

$k_{-4} = 10^{5.8} \exp(-22,800/RT) \text{ liter/mole sec.}$ The A factor $10^{5.8} \text{ liter/mole sec}$ is not unreasonable for a bimolecular reaction. Hence, the molecular elimination reaction (A) cannot be eliminated.

If the non chain radical mechanism (B) is correct, then the measured activation energy, 40.3 KCal/mole , is equal to the bond dissociation energy for the first Cl-F bond in ClF_5 . This value seems reasonable since the average bond energy in ClF_5 is 36 KCal/mole ⁵. Further support for the non chain radical mechanism is given by the generalization of Benson and DeMore⁶ that the A factor of unimolecular reactions involving the splitting off of atoms are in the range of 10^{14} to 10^{15} sec^{-1} .

It now remains to discuss the recent photochemical investigation by Krieger et al.²

They studied the kinetics of the photochemical formation of ClF_5 from ClF_3 and F_2 ($365 \text{ m}\mu$, $16-70^\circ$) and obtained the complex rate expression:

$$\frac{d(\text{ClF}_5)}{dt} = k I_a \left[\frac{k'(\text{ClF}_3)}{M} + 1 + \frac{k''}{M} \right]^{-1}$$

Their somewhat unusual mechanism involves the formation of an activated ClF_5 molecule which can (1) be collisionally deactivated to ClF_5 , (2) react directly with ClF_3 to form 2 ClF_4 radicals, or (3) split into $\text{ClF}_4 + \text{F}$. In order to explain their observed results (quantum yield dependent on inert gas pressure and on ClF_3 pressure), all three of these processes must occur to an appreciable extent in each of their experiments.

These photochemical results indicate that the ClF_5 activated molecule decomposes more rapidly than classical theory would predict. Also, the thermal decomposition of ClF_5 should be pressure dependent and accelerated by the presence of the product ClF_3 .

The thermal and photochemical results can be shown to be compatible in two ways. First, it can be calculated from the photochemical rate constants that the accelerating effect of ClF_3 would not be sufficient to appreciably affect the first-order plot shown in Fig. 1. Thermal experiments would have to be run with added ClF_3 and at various total pressures to determine if the decomposition is dependent on the

7. N. N. Semenov, "Some Problems in Chemical Kinetics and Reactivity," Volume I, Princeton University Press, Princeton, New Jersey, 1958, p 29.

concentration of ClF_3 and added inert gases.

If it turns out that the thermal decomposition rate is unaffected by added ClF_3 and inert gases, it could be argued that the activated complex in the photochemical reaction differs in average energy from the thermally-formed activated complex. The fluorine atoms formed in the photochemical decomposition of F_2 must contain considerable translational energy since there are no accessible electronic states. If a portion of this translational energy is converted to internal energy in the ClF_5 complex ($\text{F} + \text{ClF}_4 \rightarrow \text{ClF}_5^*$), the stability of the complex would be greatly reduced. For example, an additional 10 KCal/mole of activation energy would decrease the predicted half-life of the complex from about 10^{-8} to about 10^{-10} sec, and might also account for its reactivity toward ClF_3 .

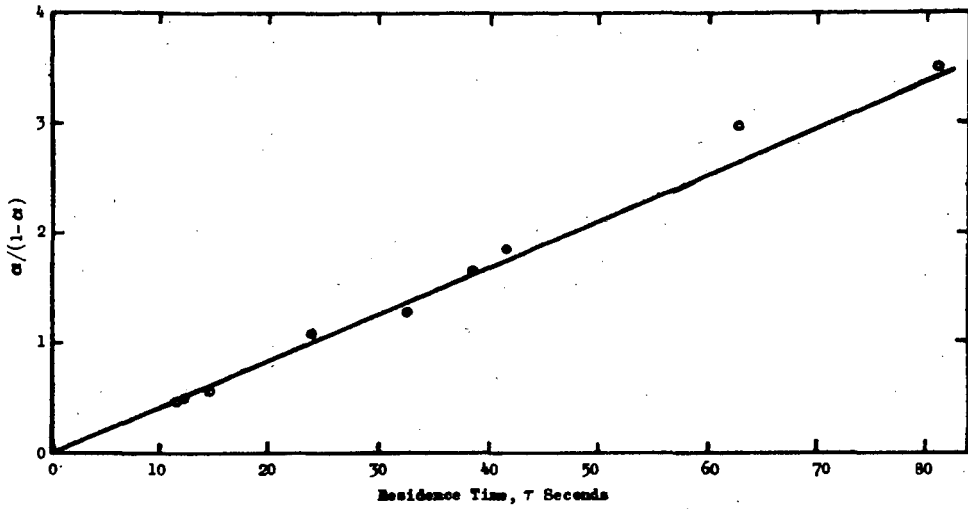


Figure 1. First-Order Plot of ClF_5 Decomposition Data at 293 C

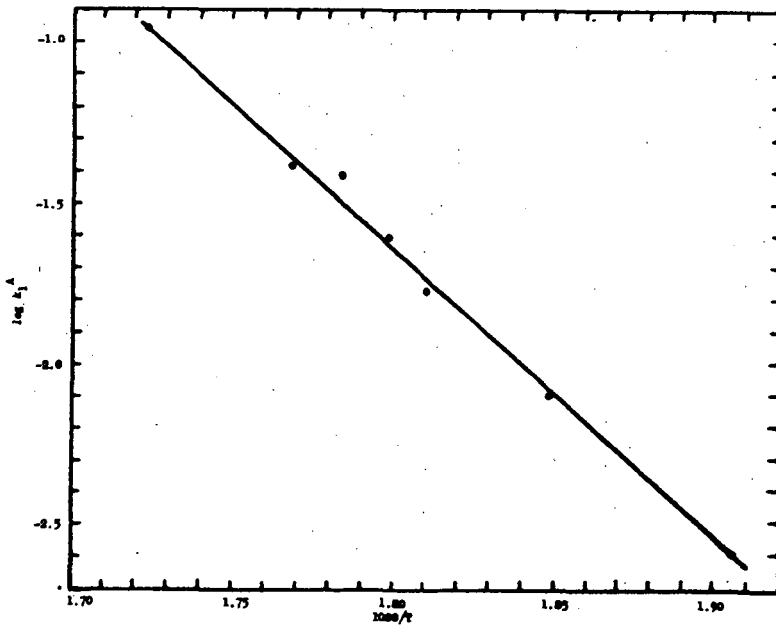


Figure 2. Arrhenius Plot

Table 1. Experimental Kinetic Data for the Pyrolysis of Gaseous
Chlorine Pentafluoride

Temp, °C	τ , sec	Fraction Reacted, α	k_1 , sec ⁻¹	k_1^A , sec ⁻¹
252.2	24.9	0.068	0.00292	0.00260
252.2	113.0	0.254	0.00300	
252.2	281.5	0.375	0.00213	
252.2	449.0	0.525	0.00246	
268.5	196.8	0.612	0.00803	0.00803
279.4	36.2	0.381	0.0170	0.0164
279.4	115.3	0.646	0.0158	
283.2	23.6	0.371	0.0250	0.0251
283.0	36.3	0.477	0.0252	
287.4	24.4	0.465	0.0357	0.0385
288.2	40.4	0.625	0.0413	
287.4	42.4	0.629	0.0398	
287.6	55.0	0.716	0.0459	
291.8	11.9	0.312	0.0380	0.0417
291.5	24.1	0.499	0.0413	
293.0	11.6	0.312	0.0391	
293.0	14.6	0.364	0.0394	
293.3	32.4	0.570	0.0408	
293.0	38.4	0.624	0.0432	
293.5	41.7	0.658	0.0462	
293.0	62.8	0.749	0.0476	
294.0	81.3	0.790	0.0464	
307.5	7.96	0.433	0.0959	0.113
306.8	9.76	0.529	0.115	
307.0	11.93	0.595	0.123	
307.5	12.9	0.583	0.109	